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W.K. Schroll, V.V. Prabhu, E.W. Prohofsky, and L.L. Van Zandt

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PHONON INTERPRETATION OF INELASTIC
NEUTRON SCATTERING IN DNA CRYSTALS[#]

by

W.K. Schroll, V.V. Prabhu,
E.W. Prohofsky, & L.L. Van Zandt

Department of Physics
Purdue University
W. Lafayette, Indiana 47907

Abstract: The calculated spectrum of longitudinal compressional waves
on DNA polymer chains is shown to be in excellent agreement with
recently performed inelastic neutron scattering measurements in
hydrated, oriented DNA crystals. This opens up a previously unexplored
frequency regime of DNA science and establishes the validity of the
phonon, extended wave description of DNA elementary excitations in
this region.

November 6, 1987

That DNA polymer in fibers and films undergoes standing wave oscillations has been established for some time now. Brillouin scattering measurements clearly show q conservation corresponding to waves propagating along the polymer chain.(1) Similarly, Raman scattering and infrared absorption studies show sharp resonance peaks in the range above 400 cm^{-1} corresponding to molecular vibrations of the polymer. (Whether or not these infrared resonances arise from standing wave modes is of lesser importance or in some cases not even a well defined question owing to the very low group velocities characteristic of the optical region.)

The frequency region between the upper end of the microwave spectrum around 100 gigaHertz and the extreme far infrared at 400 cm^{-1} has been *terra incognita* until now, because of the high absorption of water in this range. It is, therefore, of great interest that Grimm, Stiller, Majkrzak, Rupprecht and Dahlborg(2) (hereinafter GSMRD) have recently succeeded in preparing sufficiently large oriented samples for performing inelastic neutron scattering experiments. They have seen acoustic-type oscillations of the polymer chains in the teraHertz region. They have thereby extended the top of the observed frequency range by over an order of magnitude; logarithmically speaking, their observations are squarely in the middle of the unknown region. Of additional interest is the fact that their observations are not of neutrons scattered directly off of the phonons but rather off of their Brillouin zone image, the satellite peak to G = (0,0,10) . In this way, they have firmly established the validity of q conservation - the true extended wavelike nature of the excitations - in this range.

Our group has been calculating DNA phonon spectra for some considerable time. Our results have always shown a complex mixture of optical bands crossing the frequency and wave number range explored by the GSMRD experiments. It is therefore gratifying to be able to report

that we can give an accurate quantitative account of the GSMRD results from our theory. Basically, the waves observed by GSMRD are

longitudinal compressional oscillations moving along the polymer chain. The relation between ω and q is approximately linear, although projected back to zero q, the spectrum does not pass through $\omega = 0$.

Because of the non zero intercept of the q = 0 extrapolation, GSMRD proposed an optical-like form for the excitations they were measuring. The correct interpretation is rather that since the measurements could not sample the true q = 0 limit, they show only an approximate tangent to a dispersion curve that actually has a gentle downward curvature. A glance at Figure 1 shows how this produces the non zero intercept.

The neutrons are scattered coherently by the nuclei of the DNA which, because of their motion under phonon excitation act as moving sources for the scattered neutron waves. Hence the reemergent neutrons are Doppler shifted by the moving regions of higher density, phonons of compressional wave character. Figure 1 shows, among other things, our computed spectra for the relevant portions of the phonon dispersion. In the $\omega = 0$, q = 0 limit, the upper acoustic branch is of compressional wave character, i.e. showing longitudinal motion of a base pair as a whole unit. (The lower frequency acoustic branch is torsional in character.) The optical branches of the spectrum at q = 0 are characterized by various relative motions of the atoms within a single base pair.

As we come away from q = 0, the acoustic branch motions begin to include some base pair distortions, while the optical branches come to include some compressional wave character. Where the

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acoustic branch would cross the first optical branch, the compressional character continues across the gap. As q is increased further, the compressional character continues upward in frequency moving through and dispersed among the optical phonon branches of the spectrum. The data points of the GSMRD measurements all lie in this upper region and are - technically - from optical excitations, but in fact arise from the extended sound spectrum.

The second feature of Figure 1 to note is the dotted curve beginning among the acoustic branches at $\omega = 0$, $q = 0$ and gradually curving over as it rises. This curve does not correspond to any phonon branch, but rather is a composite formed from all the branches. The inelastic scattering amplitude of neutrons by phonons of any one branch will be in proportion to its component of compressional wave character. This is calculated as

$$C(q,j) = <q(j)|Q> = \sum_{i=1}^{N} q_i^*(j) \, Q_i \tag{1}$$

$q_i(j)$ is the relative motion (mass weighted) of the ith atomic coordinate within a single base pair for a phonon in the jth spectral branch; Q_i is the similar motion for a pure z translation of the base pair. The sum extends over the $N = 123$ cordinates of a G-C base pair. The $q_i(j)$ are found as the **eigenvectors** of the linear system

$$[B^+(q)fB(q) - \omega(q,j)^2 E]q(j) = 0 \tag{2}$$

In this, E is the unit 123x123 matrix, f is a matrix of force constants between internal atomic coordinates, and B(q) is a geometrical matrix relating internal coordinates to Cartesian

coordinates. $\omega(q,j)$ is the frequency of the phonon and hence the frequency shift of the neutron scattered by this phonon. The dispersion curves of Figure 1 are the complete set of eigenvalues $\omega(q,j)$ computed for a mesh of values of q.

The intensity of scattered neutrons, the count rate, will comprise, for a given q, contributions from all phonon branches for which $C(q,j)$ does not vanish. However, as good as the neutron scattering data of GSMRD are, they can not be expected to resolve the individual branches of the phonon spectrum. Hence we expect to see neutrons scattered with a distribution of final energies, or frequencies, shifted from the major, elastic (0,0,10) peak by

$$\omega_m(q) = \sum_{j=1}^{N} \omega(q,j) \, |C(q,j)|^2 \tag{3}$$

The width of the scattered neutron distribution must be at least $\sigma(q)$,

$$\sigma(q)^2 = \sum_{j=1}^{N} [\omega(q,j) - \omega_m(q)]^2 \, |C(q,j)|^2 \tag{4}$$

The $\omega_m(q)$ are plotted as the dotted curve of Figure 1, and the indicated error bars are the values of $\sigma(q)$. As a practical matter, the indicated sums in equations (3) & (4) were only extended over the lowest 10 phonon bands, no higher terms' being necessary.

The last feature of Figure 1 to which we call attention is the series of crosses lying along our calculated neutron scattering peaks, $\omega'_m(q)$. These are points taken from the contour plot of reference (2), presumably the best summary of all their results. The agreement is seen to be excellent.

An interesting feature of the theoretical curve, $\sigma(q)$, is that in the regions where the compressional character is crossing the gap from one band to another, the error bars "fatten out". Where $\omega(q,j)$ falls relatively farther from a crossing, the error bars can be drawn somewhat narrower. Unfortunately, the data are not quite sufficiently close together to determine if this feature is actually present in the experiments, although there is some hint of it.

We have elsewhere described at considerable length the contributions to the eigenvalue/eigenvector problem we solve to get the $\omega(q,j)$ and $q_i(q,j)$ (3). Some appropriate modifications in the parameters have been made for the current calculation which bear describing. The force constant matrix, f, in equation (2) is composed of several contributions. First are the direct interactions between covalently bonded neighbors in the chemical structure. These have been determined by the process of "refinement"(4) using the higher frequency infrared data that have long been available for DNA and its chemical subunits. In addition, f contains "long range", non bonding interactions. These are individually much weaker than the covalent forces, but, falling off much more slowly at long distances, are far more numerous. Consequently, the "long range" force constants come to dominate the dynamics for long wavelength phenomena such as compression waves(5). An important aspect of the long range interactions is that they are mediated by the presence of the considerable amounts of water in the polymer structure and the immediate surroundings. Hence the dielectric constant of water appears in the expression for these force constants.

The proper dielectric constant to use for water mediated interactions depends upon the frequency range of the experiments one wishes to interpret. Near $\omega = 0$, ϵ_w is approximately $81\epsilon_o$.

The coefficient, 81, is frequency dependent, a dependence arising out of a rotational relaxation process having a time constant in the picosecond range for bulk water. An additional complication comes from the fact that the water surround of DNA is not bulk water, but strongly modified water.(6) In particular the dipolar rotations are much hindered in this "hydration shell" and the corresponding relaxation is lengthened by at least an order of magnitude. The hindered, lengthened relaxation time has recently been observed and measured by Lindsay.(7)

The GSMRD neutron scattering results refer to a frequency range well above the characteristic hindered relaxation frequency of hydration water (which frequency lies in the range of a few gigaHertz). The water molecules do not rotate on the time scale of these phonons, and hence a much smaller dielectric constant is appropriate. We have used a value of $9\epsilon_o$ for the curves of Figure 1. This value for ϵ_w, if carried back down to low frequencies where the earlier Brillouin scattering measurements were made(1), results in an erroneously high value for the speed of longitudinal sound on the DNA, some 5.9×10^3 m/sec. The very lowest frequency regions of Figure 1 must be viewed with these reservations in mind.

We are encouraged both by the manifest utility of inelastic neutron scattering to explore the elementary excitations of DNA in this heretofore inaccessible frequency range. We are optimistic that further progress of neutron scattering technique may make possible the observation of waves of characters other than merely compressional. We also find it gratifying that the phonon/normal mode analysis seems to provide so useful a theoretical framework for the interpretation of the experiments in this range.

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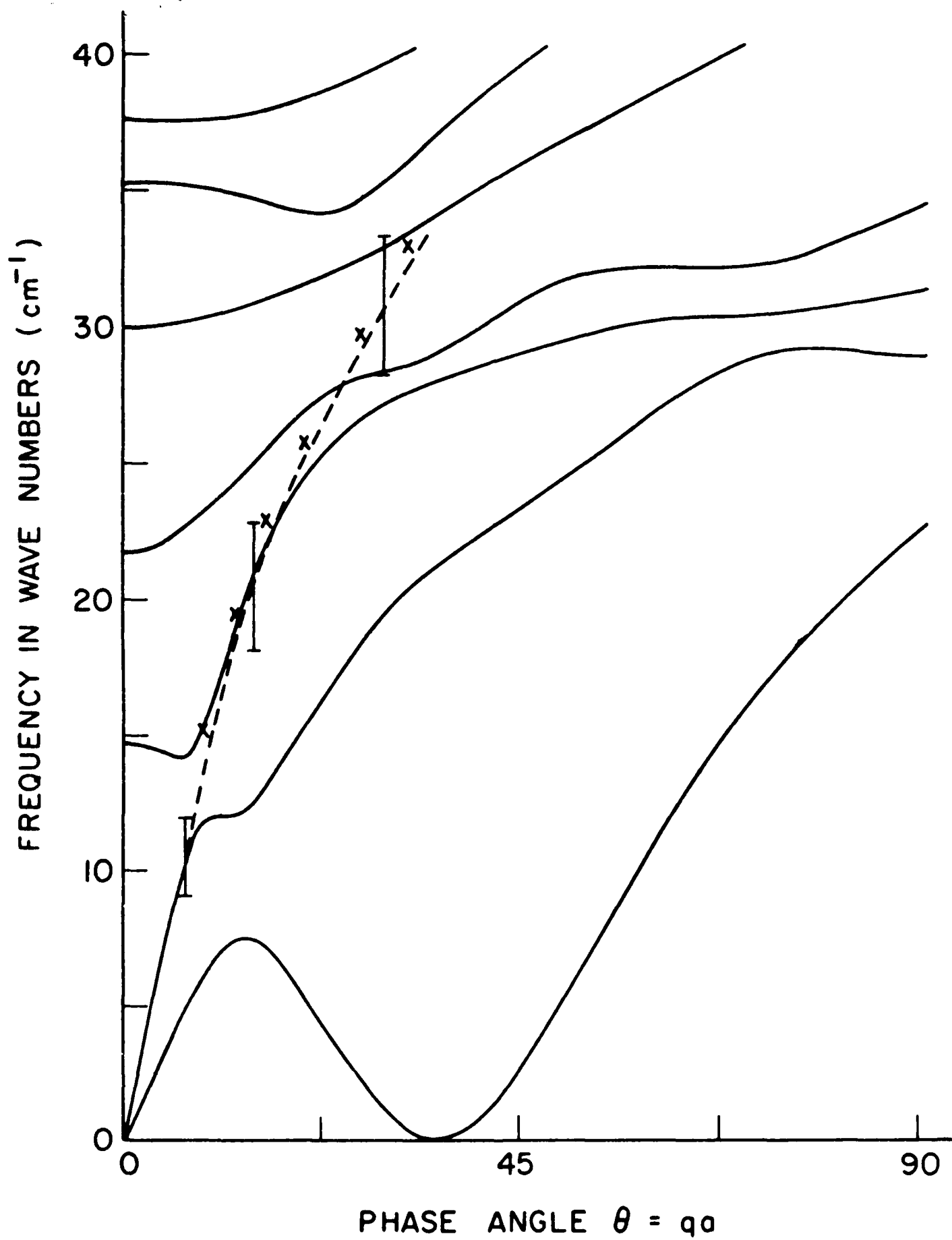(7) N.J. Tao, S.M. Lindsay, & A. Rupprecht, *Biopolymers 26*, 171 (1987).

FREQUENCY IN WAVE NUMBERS (cm^{-1})

PHASE ANGLE $\theta = qa$

Figure Caption:

Phonon excitation spectrum of DNA - poly dG:poly dC - in the teraHertz frequency range. Solid lines are the acoustic and optical branches of the vibration spectrum; the dotted line shows the mean weighted center of the longitudinal compressional wave oscillations. Error bars give the rms half width of the compressional waves computed as described in the text. Crosses are experimental measurements of density oscillations as obtained from reference (2).

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